

Theoretical study of intramolecular proton transfer reactions in some thiooxalic acid derivatives

Chamorro, Eduardo

Toro-Labbe, Alejandro

Fuentealba, Patricio

The intramolecular proton-transfer reactions in some thiooxalic acid derivatives $\text{HY} - \text{C}(=\text{O})-\text{C}(=\text{S})-\text{XH}$, (1) $\text{X}=\text{O}$, $\text{Y}=\text{O}$; (2) $\text{X}=\text{O}$, $\text{Y}=\text{S}$; (3) $\text{X}=\text{S}$, $\text{Y}=\text{S}$, have been studied in the gas-phase at the B3LYP/6-311+G(d,p) level of theory. Reactions are shown to proceed via a two step mechanism more than through single concerted interconversions. Four-membered transition states are involved along the oxygen to oxygen, sulfur to oxygen, and sulfur to sulfur, single proton-transfer processes. The double proton-transfer reaction in these systems is a competitive and coupled process with the conformational rearrangement through the central C-C bond. Reaction mechanisms have been discussed in terms of global and local chemical reactivity descriptors. The electronic nature of the transferred hydrogen has been explicitly examined using the topological analysis of the electron localization function (ELF). Ion-pair like transition structures with charge separations of 0.48e, 0.42e, and 0.18e have been found for